INFRARED ABSORPTION SPECTRA OF ETHYLENE CHLORHYDRIN IN THE VAPOUR STATE AND IN SOLUTION IN DIFFERENT SOLVENTS*

MONOMOHAN MAZUMDER

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32

(*Received for publication June 25, 1959*)

ABSTRACT The infrared absorption spectra of pure ethylene chlorhydrin in the vapour state at 28°C and 70°C and of its solutions in CCl_4, C_2Cl_4 and heptane have been recorded with a Perkin Elmer Model 21 spectrophotometer. It is observed that the ratio of the integrated absorption at the bands 662 cm^{-1} and 750 cm^{-1} remains almost the same when the liquid at 28°C is converted into vapour, while the ratio diminishes considerably when the vapour is heated to 70°C. In the case of solutions in CCl_4 and C_2Cl_4 the band 750 cm^{-1} disappears, while in the case of solution in heptane no such change takes place. These results have been explained on the assumption that in the liquid state almost all the molecules are in the associated state forming two types of dimers one through the OH .Cl bond and the other through the H-O. H bond.

INTRODUCTION

Mizushima *et al* (1939) had earlier studied the infrared absorption spectrum of ethylene chlorhydrin in the vapour state and observed three absorption maxima due to the second harmonic of the OH vibration. They assigned two of them to one molecular form and the remaining one of much lower frequency to the other. In the latter form the hydroxyl hydrogen was assumed to be coupled with the chlorine atom to form the cis configuration and the alternative form, in which the hydroxyl group was free, was considered to be the trans configuration. In the liquid state they observed only one absorption maxima and assigned it to the cis configuration. The absence of the trans configuration in the liquid state was explained by them on the assumption that the molecules of such configuration form intermolecular hydrogen bond so that the absorption due to the OH group is depressed. Later, by studying the Raman spectrum of ethylene chlorhydrin in the liquid and solid states Mizushima *et al* (1940) assigned the line 662 cm^{-1} to the trans configuration and the line 751 cm^{-1} to the gauche configuration of the molecule. In the liquid state the ratio of intensities of the lines 751 cm^{-1} and 662 cm^{-1} was found to be about 0.7. Again, Mizushima *et al* (1951) studied the infrared absorption spectrum of this compound in the vapour state at different

*Communicated by Prof. S. C. Sirkar

temperatures ranging from 82°C to 250°C and found the ratio of intensities of the absorption bands 760 cm^{-1} and 669 cm^{-1} to change from 0.551 to 0.848 with the change of temperatures mentioned above.

The Raman spectrum of the vapour of the substance at 130°C and 180°C studied by Mazumder (1955) showed that the intensity-ratio of the two lines 750 cm^{-1} and 662 cm^{-1} is about 1 : 1 at 130°C and 5 : 1 at 180°C. These results are not in agreement with those for the infrared spectra reported by Mizushima *et al* (1951). In order to understand the cause of this discrepancy and also to find out the influence of intermolecular forces on the ratio of population of the two configurations of the molecule, the infrared absorption spectra of ethylene chlorhydrin in the vapour state at 28°C and about 70°C, liquid state at 28°C and also of its solution in different solvents have been investigated and the results have been compared with those reported by previous authors.

EXPERIMENTAL

The infrared absorption spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer. Compensation cells containing pure solvents were used in the reference beam to balance the absorption due to the solvents in each case while the spectra due to the solutions were recorded.

Chemically pure ethylene chlorhydrin obtained from B.D.H. was dehydrated and fractionated. The solvents were also of purest quality. The absorption spectra of the pure liquid were recorded by using very thin films of the liquid enclosed between two NaCl discs. The thickness of the sample cell containing solutions was about 2% larger than that of the compensating cell used in the reference beam

A 10-cm cell containing a few drops of ethylene chlorhydrin in a side tube was used to record the absorption spectrum of the vapour. In this case also a compensating cell was used. The apparatus was balanced very carefully till the CO_2 bands due to atmospheric carbon dioxide were absent in the record. The C-Cl bands due to the solvents were also absent in the test records when only either CCl_4 or C_2Cl_4 was introduced in the cells in both the beams

RESULTS AND DISCUSSION

The absorption curves due to ethylene chlorhydrin in the liquid state, in the vapour state at 28°C and about 70°C and those of the solutions in CCl_4, C_2Cl_4 and heptane are reproduced in figures 1-5 and 7 respectively. The frequencies of the bands in the spectra are given in Table I.

It can be seen from Table I as well as figure 1(b) that in the liquid state the band due to OH valence oscillation is many times stronger than the two bands at 2960 cm^{-1} and 2880 cm^{-1} due to CH valence oscillations and it extends from 3100 cm^{-1} to 3650 cm^{-1} with the broad maximum at 3360 cm^{-1} and a low inflexion

TABLE I

Frequencies of the absorption bands in the spectra in cm^{-1}

Pure ethylene chlorhydrin		Solution of ethylene chlorhydrin		
Liquid	Vapour	in CCl_4	in C_2Cl_4	in heptane
662 (3)	662 (2)	662 (5)	660 (5)	660 (3)
740 (2)	750 (1)			750 (2)
840 (2)	840 ($\frac{1}{2}$)	842 (1)	840 (1)	840 ($\frac{1}{2}$)
930 (5)	920 (2)	925 (4)	920 (1)	920 (2)
1025 (12)	1035 (10)	1030 (8)	1030 (8)	1025 (12)
1065 (15)	1060 (15)	1065 (16)	1065 (20)	1065 (15)
1160 (1)	1180 (2)	1160 (0)		1180 (1)
1240 (1)		1190 (0)	1195 (1)	
1295 (4)	1285 (2)	1295 (3)	1290 (4)	1280 (2)
1380 (0)	1380 (3)	1380 (1)	1385 (2)	1380 (1)
1430 (3)	1430 (0)	1430 (3)	1430 (3)	1430 (1)
2800 (3)	2800 (4)			
2950 (5)	2950 (6)			
3350 (15b)	3400(1b)			
3600 (3)	3640 (2)			

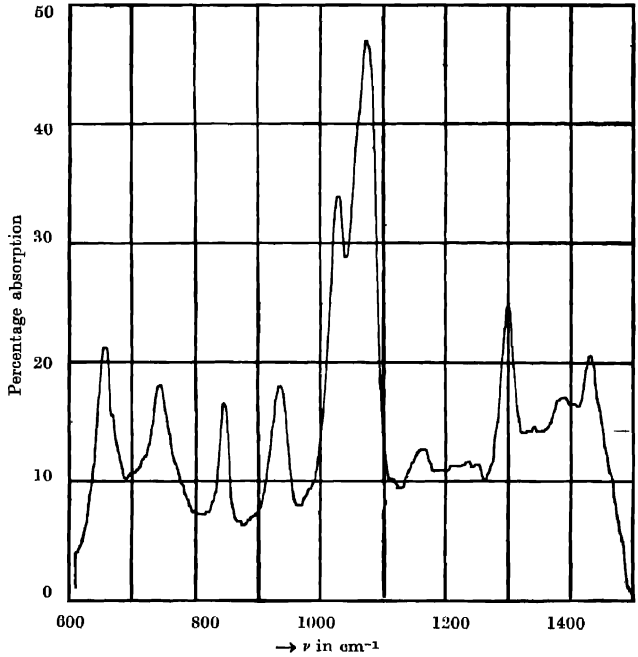

Fig. 1(*a*). Infrared absorption curve of thin film of pure ethylene chlorhydrin formed between two NaCl discs.

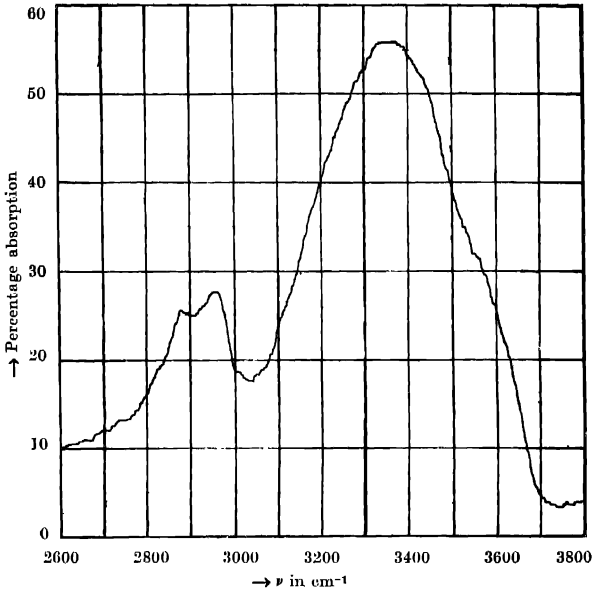

Fig. 1(*b*). Infrared absorption curve of thin film of pure ethylene chlorhydrin formed between two NaCl discs.

at 3550 cm^{-1}. On the other hand, in the spectrum due to the vapour [figure 2(b)] the OH band is very weak compared to the CH_2 bands, but it consists of one sharp peak at 3640 cm^{-1} and a weaker but broader band extending from 3200cm^{-1} to 3500 cm^{-1}. Thus it is evident that the OH band with its maximum at 3360 cm^{-1} observed in the spectrum due to pure liquid is almost absent in that due to the vapour. This conclusion is not in agreement with that drawn by Mizushima *et al*, (1939) from the results of investigation of the second harmonic of the OH bands in the near infrared region.

Table I also shows that the 1430 cm^{-1} band due to CH_2 deformation oscillations in the liquid becomes remarkably weaker, whereas the band at 1380 cm^{-1} becomes stronger in the vapour state. The ratio of the integrated absorption at the two bands 662 cm^{-1} and 750 cm^{-1} due to the vapour at 28°C is, however, almost the same as that in the case of the pure liquid. The values of the ratio observed in the absorption curves due to the three solutions given in Table I are of great help in determining the causes of these changes.

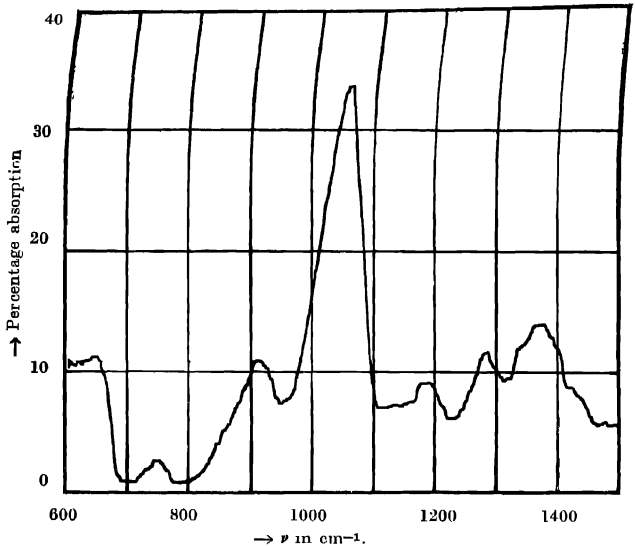

Fig. 2(*a*) Infrared absorption curve of ethylene chlorhydrin in the vapour state at 28°C (cell 10 cm).

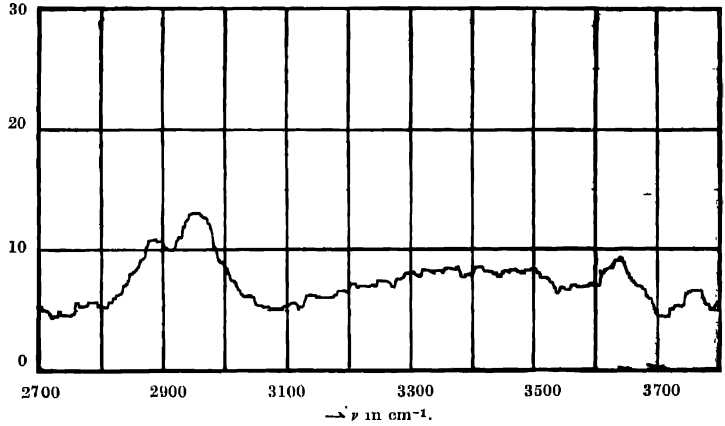

Fig. 2(*b*). Infrared absorption curve of ethylene chlorhydrin in the vapour state at 28°C (cell 10 cm).

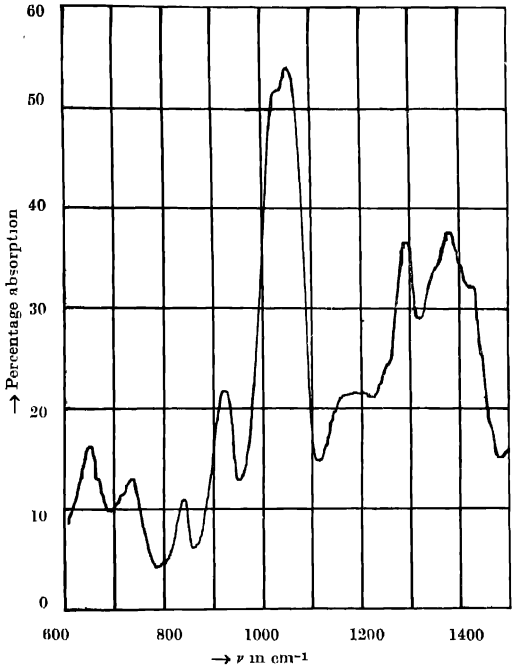

Fig 3. Infrared absorption curve of ethylene chlorhydrin in the vapour state at about 70°C (cell 10 cm).

A comparison of the curves in figures 1, 4 and 5 show that when the pure liquid is dissolved either in CCl_4 or in the C_2Cl_4 the band 750 cm^{-1} disappears and the bands 842 cm^{-1} and 1030 cm^{-1} become weaker, while the bands 662 cm^{-1}, 1065 cm^{-1} and 1380 cm^{-1} become stronger. Thus the latter three bands are to be assigned to one configuration of the molecule. The frequencies 662 cm^{-1}, 845 cm^{-1} and 1035 cm^{-1} were, however, assigned by Mizushima *et al* (1951) to the gauche configuration and the frequencies 750 cm^{-1} and 1065 cm^{-1} to the trans configuration It is quite evident from figures 1 and 4 that the frequencies 750 cm^{-1} and 1065 cm^{-1} cannot be assigned to the same configuration of the molecule. On the other hand, if it is assumed that the band 1065 cm^{-1} is produced by the trans configuration, the band 662 cm^{-1} is also to be assigned to the same configuration.

In the solution in CCl_4 or C_2Cl_4 the formation of OH. .Cl bond between the OH group of ethylene chlorhydrin molecule and the chlorine atom of the solvent molecules is highly probable. In that case the frequency 662 cm^{-1} is to be

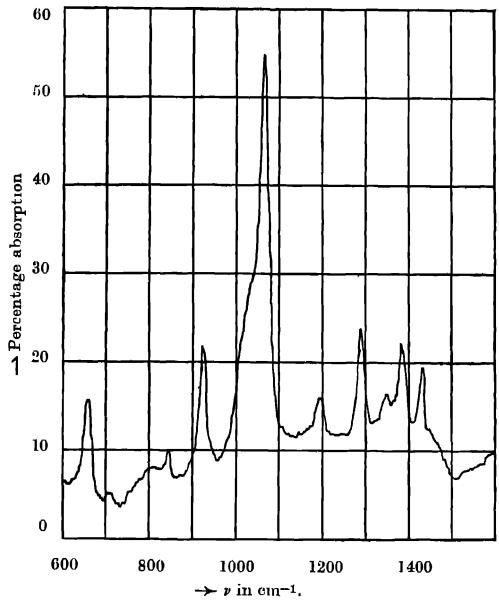

Fig. 4. Infrared absorption curve of 2% solution of ethylene chlorhydrin in CCl_4 (cell 0.1 mm).

assigned to such associated molecules. The disappearance of the Raman line 750 cm^{-1} in the spectrum due to the solid state of ethylene chlorhydrin (Mizushima *et al*, 1940) indicates that the molecules in the associated state yields the frequency 662 cm^{-1}, while the weakening of the Raman line 662 cm^{-1} in the vapour state (Mazumder, 1955) shows that the single molecules produce the frequency 750 cm^{-1}, because single molecules are expected to predominate in the vapour. In the liquid state we can expect the formation of dimers through OH. .Cl bond between two neighbouring molecules [figure 6(a)]. Also some of the molecules may become associated through H-O..H bond [figure 6(b)] as pointed out by Pauling (1945) in the case of *o*-chlorophenol. The nature of the OH band at 3360 cm^{-1} given by the liquid in the present investigation appears to be similar to that of the OH band exhibited by *o*-chlorophenol (Sirkar *et al*, 1958) and this may confirm the assumption made regarding the formation of dimers through H-O..H bond.

Table 1 shows further that in the liquid state the ratio of the integrated absorption at the bands 662 cm^{-1} and 750 cm^{-1} is about 3: 2 and in the vapour state at 28°C this ratio remains practically unchanged. To explain the results

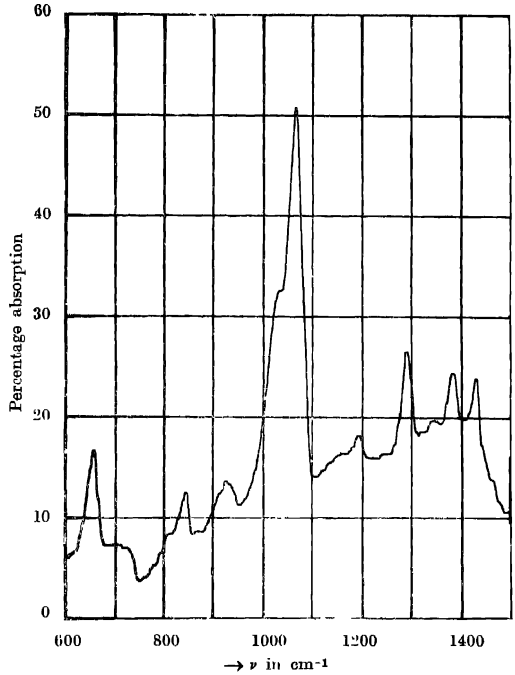

Fig. Infrared absorption curve of 2% solution of ethylene chlorhydrin in C_2Cl_4 (cell 0 1 mm)

described above it may be assumed that the dimers formed through OH..Cl bond predominate in the liquid state and the frequency 662 cm^{-1} is assigned to the C-Cl vibration in these dimers. On the other hand, the frequency 750 cm^{-1} of C-Cl vibration in single molecules may not be affected by the formation of dimers through H–O. .H bond and the frequency 750 cm^{-1} may be assigned to the C–Cl vibration in such dimers. In the vapour state at 28°C most of the latter type of dimers may break up, while those formed through O–H . .Cl bond may persist because of greater strength of the virtual bond in this case. Thus the breaking up of the dimers formed through H–O . .H bond mentioned above is not expected to affect the ratio of the integrated absorption at the bands 662 cm^{-1} and 750 cm^{-1}. On the other hand, as the intense band at 3400 cm^{-1} due to the liquid is due to H–O. .H group, this band disappears as the group breaks up in the vapour state. This may explain the absence of the band at 3400 cm^{-1} in the spectrum due to the vapour. The weak band at 3640 cm^{-1} is the OH band due to the free single molecules.

When the temperature of the vapour is raised to 70°C, however, the height of both the peaks at 750 cm^{-1} and 1035 cm^{-1} increases relative to those of 662 cm^{-1}

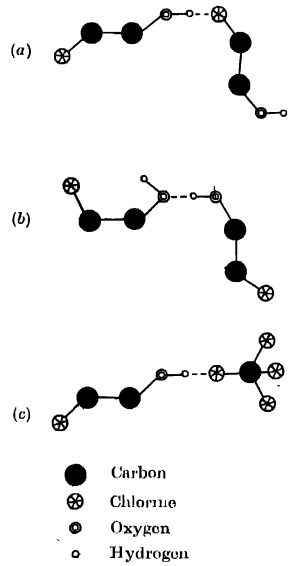

Fig. 6

and 1060 cm^{-1} respectively. This shows that the number of single molecules increases rapidly due to the dissociation of the dimers formed through O-H. .Cl bond. The results of investigation on the Raman spectra of ethylene chlorhydrin in the vapour state at 130°C and 180°C (Mazumder, 1955) show that the ratio of the intensities of the lines 662 cm^{-1} and 750 cm^{-1} becomes about 1 : 1 at 130°C and it diminishes to about 1 · 5 at 180°C. So, the latter results are in agreement with those obtained in the present investigation. It is to be pointed out, however, that the results of investigation of the dependence on temperature of the relative heights of the absorption peaks at 669 cm^{-1} and 760 cm^{-1} reported by Mizushima *et al* (1951) are not in agreement with the facts observed in the present investigation A comparison of the curves reproduced in figures 1 and 3 shows definitely that the latter curve is due to the vapour, because the band at 1430 cm^{-1} is very weak in this curve, whereas it is very strong in the curve due to the liquid. It is also found from figure 3 that the band at 750 cm^{-1} becomes much stronger at higher temperature of the vapour relative to that of the band at 662 cm^{-1}.

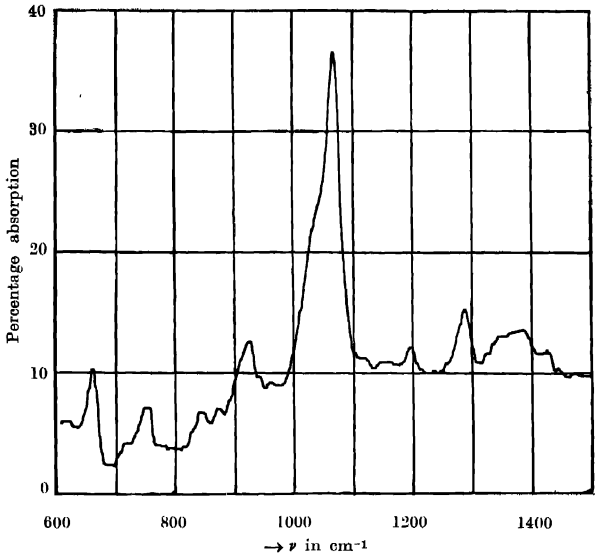

Fig 7. Infrared absorption curve of 2% solution of ethylene chlorhydrin in heptane (cell 0.1 mm).

Figure 7 shows that the relative heights of the absorption peaks at 660 cm^{-1} and 750 cm^{-1} and also at 1025 cm^{-1} and 1065 cm^{-1} due to the solution of ethylene chlorhydrin in heptane remain almost the same as in those due to the pure liquid. This result is quite in good agreement with the assumption made in the above discussions, because the hydrogen atoms of the solvent molecules cannot break up the dimers formed through OH .Cl bond

It is thus evident from the above discussions that the assignment of the frequencies 662 cm^{-1} and 750 cm^{-1} to two different configurations of ethylene chlorhydrin molecules cannot explain satisfactorily the results obtained in this investigation and that the formation of dimers in the liquid is to be postulated to explain the observed changes in the relative strengths of the two absorption bands.

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for kindly suggesting the problem and for his constant guidance throughout the progress of the work.

REFERENCES

Mazumder, M., 1955, *Ind. J. Phys.*, **29**, 361

Mizushima, S., Kutoba, A. and Morino, Y., 1939, *Bull. Chem. Soc., Japan*, **14**, 15.

Mizushima, S., Morino, Y. and Nakamura, S., 1940, *Sc. Papers I.P.C.R. (Tokyo)*, **37**, 205.

Mizushima, S., Shimanouchi, T., Miyazawa, T., Abe, K. and Yasumi, M., 1951, *J. Chem. Phys.*, **19**, 1477

Pauling, L., 1945, Nature of the Chemical Bond., p. 324.

Sirkar, S. C., Deb, A. R. and Banerjee, S. B., 1958, *Ind. J. Phys.*, **32**, 345.